

Review of Viola et al. 2025

This study offers a valuable sensitivity test for a promising new tool in alkenone paleothermometry, mass spectrometry imaging (MSI), which currently offers the highest possible resolution for U^{k}_{37} measurements in sediment. Here, MSI is applied to a well-characterized, finely-laminated sediment core from the Santa Barbara Basin (SBB). The authors describe heterogeneities in U^{k}_{37} measurements across horizontal laminae and vertical depth, using estimates of SNR to infer the upper resolution limit at which a climate signal is preserved. The use of SBB sediments offers an opportunity for excellent age constraints and the description of signal preservation in temporal terms. This approach has a number of valuable applications in alkenone paleothermometry and is helpful for those looking to apply MSI in a statistically rigorous way. My background is in organic geochemistry and my comments focus mainly on the use of the alkenone U^{k}_{37} proxy in sediment and the overall structure and clarity of the paper. I cannot provide in-depth commentary on the quality/validity of the scanning methods used or the applied statistical analysis.

General Comments

1. The clarity of the manuscript could be improved in a few ways. First, I would recommend that the authors be much more specific about directionality when describing depth intervals, particularly given that this study explores both horizontal and vertical variability in U^{k}_{37} . For example, I find the methods section beginning at line 69 quite confusing. A “30-cm long section” of the core is used, as well as three “5-cm replicated MSI measurements” of boxcore SPR0901-05BC. Later, “5-cm subsections” are “cut into 100-um slices” (line 78). I have a hard time visualizing this workflow, and I think that the schematic in Figure 1 could be introduced sooner, referenced more, and also made clearer. I don’t quite understand what each step represents, particularly with respect to the direction of each core section and the direction of scanning. Arrows and labels would help.
2. The discussion of methods for spot-measuring alkenone compounds should be described more fully. The equation for U^{k}_{37} should be given somewhere, and I’m a bit confused about how swU^k is calculated for the spot measurements. The authors say in Line 166 that “On average, at 62% of the shots at least one of the three compounds was detected...while at least one alkenone was detected in 46% and both in 34%.” Were swU^k calculated for shots with one alkenone compound present? If so, would these values not just go to 0 or 1? Is it that the

concentrations are near the detection limits of the instrument, or is it actually possible to have a relatively high concentration of C37:2, for example, and no C37:3? If the former is true, is there any size effect bias on swUk?

3. The paper needs the age controls on the sediment core to be discussed more thoroughly. The authors, for example, identify their sediments as containing the 1761 and 1532 CE gray flood layers (Line 115), but do not provide further information on how these specific floods were identified. A supplemental figure showing stratigraphic alignment of core KC1 with previously characterized SBB sediments, or a more thorough description of the method the authors used, would be helpful for demonstrating the validity of these flood ages to the reader. Further, the authors describe that SBB sediments are generally “varved, laminated, or bioturbated” (Line 112), but do not thoroughly describe the banding characteristics of the core section KC1. This creates confusion when the authors translate from depth to temporal scale.

In line 117, the authors begin by saying that only a linear interpolation age model is possible between 1761 and 1532, but later say that in core KC1, they detect SNRs “around 1 at interannual resolution, increasing to 3 at subdecadal resolution. The extracted noise component shows no dependence on time scale” (Line 315). The validity of this statement relies on there being an age model with annual to decadal resolution and an in-depth description of such age constraints. Ultimately, I’m confused as to how the authors translate between depth and age scales in core KC1.

4. How do U_{37}^k values derived from MSI scanning methods compare with measurements from traditional laboratory extractions and GC-MSD/GC-FID/HPLC measurements? I think that this technique is new enough that it warrants more thorough discussion/citation of previous validation studies.

5. In line 301, the authors speculate as to the causes of spatial heterogeneity in alkenone swUk and posit that this signal may be reflecting real variability (as opposed to measurement error), given that “water column and sediment trap data display a broader range of U_{37}^k values than core tops, and lab cultures have been shown to exhibit even greater variability...” I would appreciate a quantitative comparison between the variability captured by the MSI scanning techniques and those in the aforementioned settings. Is the degree of heterogeneity captured by MSI physically reasonable? I would particularly appreciate a direct comparison to sediment trap

data, given that the authors are investigating individual laminae which would accrete on somewhat comparable timescales. Based on previous studies, what is the maximum amount of noise that might reasonably be explained by variability in alkenone production about the same SST? What might be the approximate range of SST values that might be reasonably integrated over a single season? How do you expect water column and sedimentation processes to smooth (or not smooth) variability of alkenone production in the photic zone? It seems that if the observed spatial heterogeneity is *not* a product of measurement error, signal noise may contain valuable information that would be of interest to paleoclimatologists looking to apply MSI. I think that the paper could be improved if these possibilities were explored more thoroughly. I would recommend that Supplementary Figure 5 be brought into the main body of the paper and discussed.

Corrections

The manuscript contains a number of grammatical and typing errors and should be proofread, paying particular attention to comma and hyphen usage, spelling, and the use of “that” versus “which.” Examples are presented for the first 100 lines and the Figure 2 caption, along with one citation recommendation.

L30 - I suggest the authors use “longer” timescales rather than “slower”

L31 - There is an extra space between in “dynamics of”

L31 - Grammatical error in “Similarly, understanding of the long-term dynamics **of phenomena like monsoon** or El Nino-Southern Oscillation (ENSO), results...”

L38 - Hyphen needed for “long-enough”

L40 - Needs an additional comma. “This might, however, not be the case...”

L42 - Extra space between carriers and the following period

L43-44 - Needs additional comma. “Such heterogeneity may arise during signal production, for example, due to...”

L46 - I would drop the apostrophes/quotations for ‘stratigraphic noise’

L46 - Correct to “archives”

L52 - Should cite Brassell et al., 1986

L56 - Remove comma in “annual varve couplets, and”

L57-59 - “for their preservation under low-oxygen conditions that reduce bioturbation” should be amended to “for their preservation under low-oxygen conditions, which reduce bioturbation” unless the authors mean to say that some low-oxygen conditions do not reduce bioturbation.

Similarly, “from minimal disturbances that preserved varves...” should be clarified.

L64 - Need a comma before “which”... “individual MSI-based reconstructions, which indicate...”

L69-70 - Opening line of the paragraph is not a full sentence and needs to be clarified:

“Sediment core MV1012-001KC was retrieved by research vessel Melville during cruise MV1012 in 2012, stored and accessed at Scripps Institution of Oceanography’s cored sediment and microfossil collection.”

L70-71 - Needs an additional hyphen for “30-cm-long”. Comma usage with “named “KC1”” is incorrect. Need to change wording for the second clause of the sentence ending in “...in the following.” For example: “...referred to as KC1 for the remainder of this manuscript.”

L72 - Correct to “three 5-cm-replicated measurements” for clarity

L72 - Need commas for “of boxcore SPR0901-05BC, originally published by Alfken et al. (2020), as an example...”

L76 - Correct to “freeze-dried”

L76 - Correct spelling of “embedded”

L79 - Need a comma for “(Medite Cryostat M630), and”

L81 - “Finally, the slices were measured”... what was measured exactly?

L81 - Need a comma for “FT-ICR-MS, coupled to”

L84 - Need to adjust “in the supplements section S1”... e.g. “in section S1 of the supplemental materials.”

L84 - “For each 5 cm depth”... In some places you use a dash with 5-cm, and other times you do not. Stay consistent with one or the other; both are correct.

L88 - “adducts of the di- and triunsaturated alkenones” should be adjusted to “adducts of the di- and tri-unsaturated alkenones.”

L93 - Need a hyphen for “first-order estimation”

L184 - Need to describe the Xs in panel A in the figure caption

L184-185 - This part of the figure caption is not grammatically clear: “Maps are shown as measured, on the MSI coordinate grid, before affine transformation onto Xray coordinates, values below 1% and above 99% quantiles were removed for optimal color scaling during plotting.